UNIVERSITI PUTRA MALAYSIA

CHEMICAL AND MINERALOGICAL FORMS OF HEAVY METALS IN SEDIMENTS AT LANGAT RIVER, SELANGOR

NUR ALIAA SHAFIE

FPAS 2013 4

CHEMICAL AND MINERALOGICAL FORMS OF HEAVY METALS IN SEDIMENTS AT LANGAT RIVER, SELANGOR

NUR ALIAA SHAFIE

MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2013

CHEMICAL AND MINERALOGICAL FORMS OF HEAVY METALS IN SEDIMENTS AT LANGAT RIVER, SELANGOR.

By

NUR ALIAA SHAFIE

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master Science

March 2013

COPYRIGHT

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree Master of Science

CHEMICAL AND MINERALOGICAL FORMS OF HEAVY METALS IN SEDIMENTS AT LANGAT RIVER, SELANGOR.

By

NUR ALIAA SHAFIE

March 2013

Chairman: Ahmad Zaharin Aris, PhD

Faculty: Environmental Studies

Langat River is one of the most important rivers in Selangor that caters drinking water sources for up to 1.2 million populations within the basin. In 2004, Langat River has been recognized as one of the Hydrology for the Environment, Life and Policy (HELP) river basin. An explanatory study was carried out at 22 sampling stations along the river. The sediment samples (0 – 20cm) were collected for metal speciation (Cd, Cu, Zn, As, Pb) using sequential extraction technique (SET) and analyzed via the inductively coupled plasma-mass spectrometry (ICP-MS). Parameters such as pH, Eh, electrical conductivity (EC), salinity, loss on ignition (LOI), cation exchange capacity (CEC) and particle size analysis (PSA) were also determined. The sediment mineralogy was determined using X - Ray diffraction (XRD). This study revealed that sediment was predominantly by Pb(150.29µg/g)>Cu(57.91µg/g)>As (37.40µg/g)>Zn (30.46µg/g)>Cd (0.061µg/g). There is a significant correlation among pH, Eh, EC, Ca^{2+}, Cu, Zn, As with Pb at r=-0.234 - 0.354 ($p<0.01$). The associations among metals (Cd, Cu, Zn and As)

with sediment characteristics variables were due to the factor that each variables poses towards the bioavailability of metals in the environment. The sediment mineralogy also played a significant role in controlling the fate of metal. The mineralogy that is dominant by quartz correlated with Zn, As and Pb at $p<0.1$ confirmed that mineralogy controlled the metals accumulation. The fractionation indicate the metals mobility were Cu>Cd>Zn>As>Pb in decreasing order. The association of Cu (94.61%) and Cd (64.80%) were described to be strongly attached with the non residual phase. This is contradicting with Zn (52.46%), As (66.43%) and Pb (92.21%) that accounted as the least mobile metals as a result of strong association with the residual phases. This suggests that Cu and Cd are more prone to the remobilization in the overlying water compared to Zn, As and Pb. The principal component analysis (PCA) exhibited salinity as the controlling factor in the river clusters separation. This is proven by the correlation of salinity with CEC, LOI, Na^{+}, Ca^{2+}, Mg^{2+}, K^{+}, Cd, Cu and Zn at PC1. This suggests that natural sources are the highest percentage of contribution (31.92%). The dendogram displayed stations LA 2, LA 3, LA 4, LA 5 and LA 8 as highly contaminated by Cu, Zn and As. This is supported by sediment quality guidelines (SQGs) that exhibited As as the most contaminated with 100% exceeding the permissible limits. Therefore, it is crucial to understand the interactions of specific metals in the sediment in order to controls the release, remobilization and absorption. These findings are expected to update the current status of the heavy metal pollution status as well as creating awareness concerning the security of the river water as a drinking water sources.

Keyword: sediment, heavy metal, sequential extraction technique, mobility.

Abstrak ini yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SIFAT-SIFAT KIMIA DAN MINERALOGI LOGAM BERAT DALAM SEDIMEN DI SUNGAI LANGAT, SELANGOR

Oleh

NUR ALIAA SHAFIE

Mac 2013

Pengerusi: Ahmad Zaharin Aris, PhD

Fakulti: Pengajian Alam Sekitar

Sungai Langat merupakan sungai yang paling penting di Selangor yang bertindak sebagai sumber air minuman untuk lebih 1.2 juta penduduk di lembangan Sungai Langat. Pada tahun 2004, Sungai Langat telah diiktiraf sebagai salah satu lembangan sungai dibawah naugan Hidrologi bagi Alam Sekitar, Kehidupan dan Dasar (HELP). Satu kajian telah dijalankan di 22 stesen persampelan di sepanjang Sungai Langat. Sampel sedimen (0 - 20cm) telah diambil untuk penspesian logam (Cd, Cu, Zn, As, Pb) melalui teknik pengekstrakan berjujukan (SET) dan dianalisis menggunakan induksi plasma spektrometri jisim (ICP-MS). Parameter seperti pH, Eh, kekonduksian elektrik (EC), kemasinan, kehilangan menerusi pembakaran (LOI), kapasiti penukargantian kation (CEC) dan analisis saiz zarah (PSA) juga telah ditentukan. Mineralogi sedimen juga telah ditentukan dengan menggunakan X-Ray pembelauan (XRD). Kajian ini menunjukkan bahawa sedimen didominasi oleh Pb(150.29µg/g)>Cu(57.91µg/g)> As(37.40µg/g)>Zn(30.46µg/g)>Cd(0.061µg/g). Pb menunjukkan hubungan yang

signifikan dengan pH, Eh, EC, Ca^{2+}, Cu, Zn pada r=-0.234 - 0.354 ($p<0.01$). Penyatuan yang signifikan diantara logam berat (Cd, Cu, Zn dan As) dan pembolehubah ciri-ciri sedimen adalah disebabkan oleh faktor yang dimiliki oleh setiap pembolehubah terhadap bioavailabiliti logam berat didalam alam sekitar. Mineralogi sedimen memainkan peranan penting dalam mengawal nasib logam. Mineralogi sedimen di Sungai Langat didominansi oleh kuarza menunjukkan kolerasi yang signifikan dengan Zn, As dan Pb pada $p<0.1$. Ini mengesahkan bahawa mineralogi mempunyai kawalan terhadap pengumpulan logam berat didalam sedimen. Penspesian menunjukkan pergerakan logam didominasi oleh Cu> Cd> Zn> As> Pb. Cu (94.61%) dan Cd (64.80%) dikenalpasti mempunyai daya tarikan yang tinggi dengan fasa bukan sisa. Ini bercanggah dengan Zn (52.46%), As (66.43%) dan Pb (92.21%) yang didapati sebagai logam berat yang paling kurang bergerak hasil daripada penyatuan yang kukuh dengan fasa sisa. Ini menunjukkan bahawa Cu dan Cd adalah lebih cenderung kepada remobilisasi di dalam permukaan air berbanding Zn, As dan Pb. Analisis komponen utama (PCA) mempamerkan kemasinan sebagai faktor kawalan yang penting didalam pemisahan kelompok sungai. Ini dibuktikan oleh korelasi kemasinan dengan CEC, LOI, Na^{+}, Ca^{2+}, Mg^{2+}, K^{+}, Cd, Cu dan Zn di PC1. Ini membuktikan bahawa sumber-sumber semula jadi adalah penyumbang kepada peratusan tertinggi di Sungai Langat (31.92%). Dendogram memaparkan stesen LA 2, LA 3, LA 4, LA 5 dan LA 8 sebagai paling tercemar oleh Cu, Zn dan As. Ini disokong oleh garis panduan kualiti sedimen (SQGs) yang menunjukkan As sebagai logam paling tercemar dengan 100% melebihi had yang dibenarkan oleh SQGs. Pengetahuan yang sangat mendalam dalam pemahaman interaksi logam tertentu adalah sangat penting untuk mengawal pelepasan, remobilisasi dan penyerapan logam berat didalam sedimen. Penemuan ini dijangka dapat mengemaskini status semasa

pencemaran logam berat serta mewujudkan kesedaran mengenai keselamatan air sungai sebagai sumber air minuman.

Kata kunci: sedimen, logam berat, teknik pengekstrakan berjujukan, mobiliti.

ACKNOWLEDGEMENTS

Alhamdulillah, I am grateful and thankful to the Almighty Allah S.W.T for giving me strength, courage, patience and determination in preparing and completing this research successfully.

I would like to express my deepest gratitude to my supervisor, Dr Ahmad Zaharin Aris for his continuous supervision, assistance, guidance, opportunity and trust for the accomplishment of this research. Other than that, I would also like to thank my co-supervisor, Prof. Dr Mohamad Pauzi Zakaria and also Dr Hafizan Juahir for their assistance, guidance and ideas in order for me to improved and beautify the research.

In addition, I wish to thank all the government agencies and staffs especially from Faculty of Environmental Studies (UPM), Department of Irrigation and Drainage (DID), Forest Research Institute Malaysia (FRIM) and Malaysian Nuclear Agency that have been assisting with the sampling campaign and also providing the laboratory equipments throughout this research. I would also like to acknowledged the Research University Grant Scheme (RUGS) Project Number 03-01-10-0890RUVot 91895 from Universiti Putra Malaysia and The Academy of Science for the Developing World (TWAS) Research Grant Agreement (GRA) No: 09-099RG/EAS/AS_C-UNESCO FR:3240231216 for financing this research. My deepest appreciation to the Ministry of Higher Education (MOHE), World Federation of Scientist (WFS) and Graduate Research Fellowship (GRF) from Universiti Putra Malaysia for the financial support in order for me to complete this research.

I would like to be grateful to my parents Shafie Bin Abdullah and Yusnani Mohd Yusof for their constant support, encouragement, financial support, prayers and for being the most understanding parents during my ups and downs. Not forgotten to my family member Nani Ilyana, Mohammad Shafeeq, Muhammad Aliff, Nur Asilla Hani, Hayati, Marek and Paridah for lending their ears and encouraging me to keep on striving for excellence. My special thanks to Mohd Fahmi for always being there in supporting, encouraging, helping, reminding and motivates me constantly.

I wish to be thankful to all my friends for their continuous support, reminders, encouragement, advice, ideas, assistance and for lending their hands other than seeing the truth in me. I dedicate this appreciation to Hazzeman, Hajar, Norazida, Lim Wan Ying, Isahak, Amar, Saiful, Nurul Afiqah, Husna, Raja Nurul Nadia, Roshide, Wan Farahein, Noorain, Looi Ley Juen, Norliza, Adamu, Farhah Amalya, Lim Ai Phing and Kamran.

There are no words that I can give other than thankful to all the assistance that I have gained in making this research to live. I believe only Allah can repay the kindness that each one have give me in order for my dreams to come true. Honestly, these experiences have been nothing but the best in my life. Last but not least, thank you to all that have significantly or insignificantly contribute to the completion of this research. Thank You.

I certify that a Thesis Examination Committee has met on 7 March 2013 to conduct the final examination of Nur Aliaa binti Shafie on her thesis entitled "Chemical and Mineralogical Forms of Heavy Metals in Sediments of Langat River, Selangor, Malaysia." in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

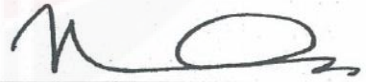
Members of the Thesis Examination Committee were as follows:

Mohammad Firuz bin Ramli, PhD
Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Chairman)

Zailina binti Hashim, PhD
Professor
Faculty of Medicine and Health Science
Universiti Putra Malaysia
(Internal Examiner)

Yap Chee Kong, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Mohd Talib bin Latif, PhD
Associate Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
Malaysia
(External Examiner)



NORITAH OMAR, PhD
Associate Professor and Deputy Dean
School of Graduates Studies
Universiti Putra Malaysia

Date: 26 June 2013

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory committee were as follows:

Ahmad Zaharin Aris, PhD
Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Chairman)

Mohamad Pauzi Zakaria, PhD
Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Member)

_____

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduates Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and it's not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

_____

NUR ALIAA SHAFIE

Date:

TABLE OF CONTENTS